

(12) UK Patent Application (19) GB (11) 2 289 680 (13) A

(43) Date of A Publication 29.11.1995

(21) Application No 9410444.5

(22) Date of Filing 25.05.1994

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(51) INT CL⁶
C09J 11/00, C08K 3/32 5/16 5/49 // C09J 11/04 11/06
11/08, (C08K 5/49 5:521)

(52) UK CL (Edition N)
C3K KEB KEZ K123 K201 K210 K222 K253 K254 K272
K274 K283 K291 K292
C3W W113 W115 W201 W203 W209 W210 W213 W219
W224 W225 W226 W303

(56) Documents Cited
WO 90/01411 A1 US 4699824 A US 4415615 A
US 4081826 A

(58) Field of Search
UK CL (Edition M) C3K KEB KEC KEF KEZ
INT CL⁶ C08K 3/32 5/34 5/3467 5/3477 5/3492 5/52
5/521 5/5397 5/5399
Online databases : WPI, CHEMLIT

(54) Flame-retardant pressure sensitive adhesives and tapes

(57) A pressure sensitive adhesive composition suitable for making tapes contains a non-halogen intumescent flame retardant. The pressure sensitive adhesive compositions may be based on adhesives including rubber based compositions, acrylic adhesive compositions and adhesive foams. Suitable flame retardants include non-halogen phosphorus/nitrogen flame retardants and a further flame retardant e.g. a halogenated retardant may also be added.

The adhesive foam may comprise hollow glass or polymeric microbubbles or may be made by frothing an adhesive.

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

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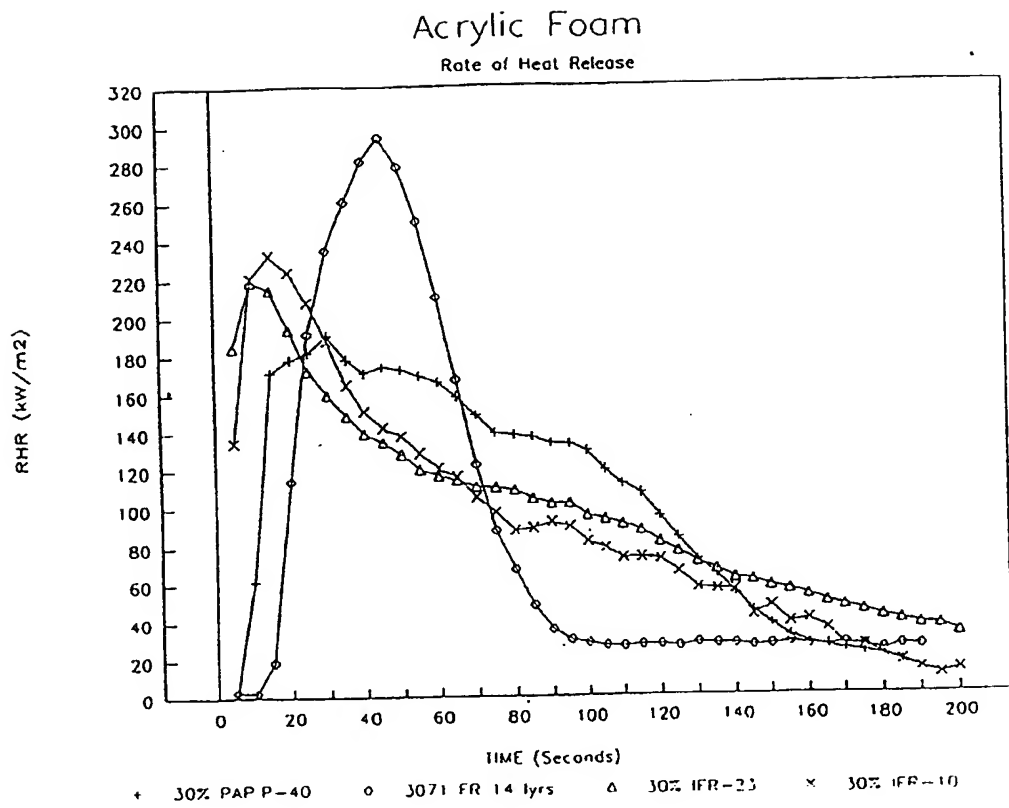


FIGURE 1

Acrylic Foam

Rate of Heat Release

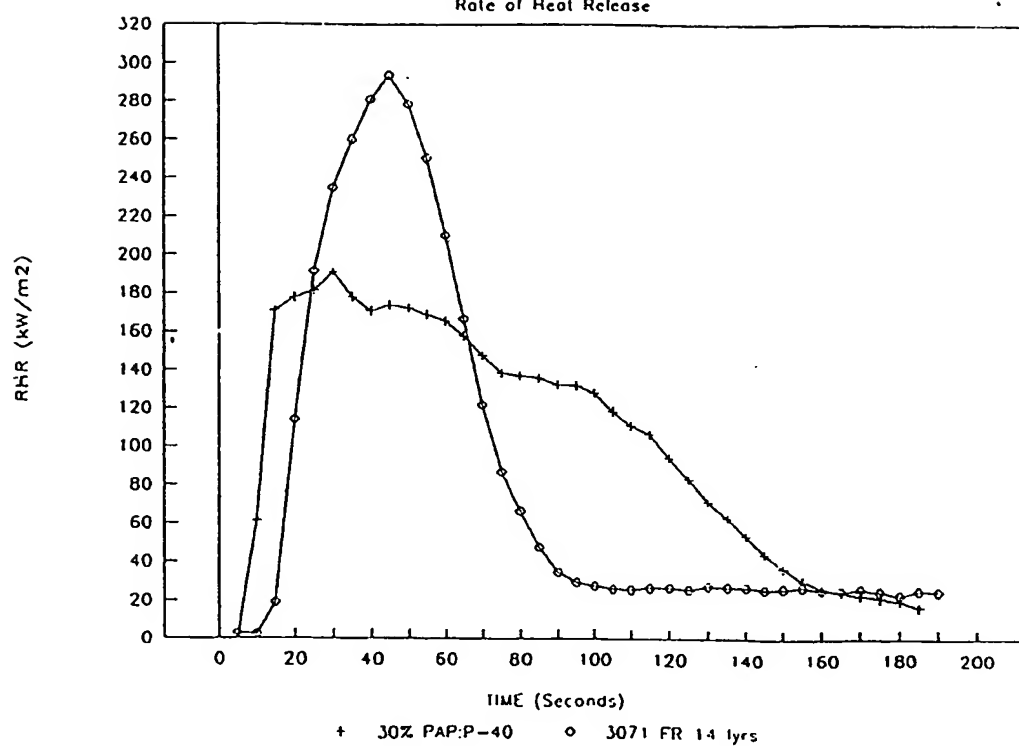


FIGURE 2

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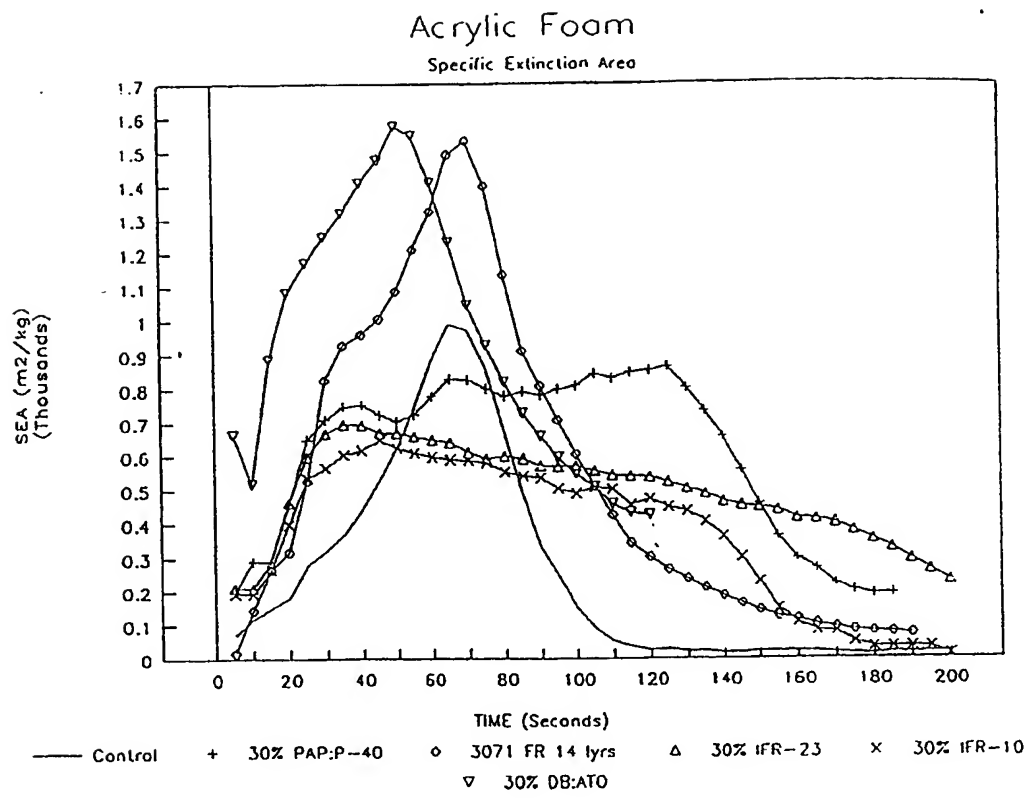


FIGURE 3

Acrylic Foam

Specific Extinction Area

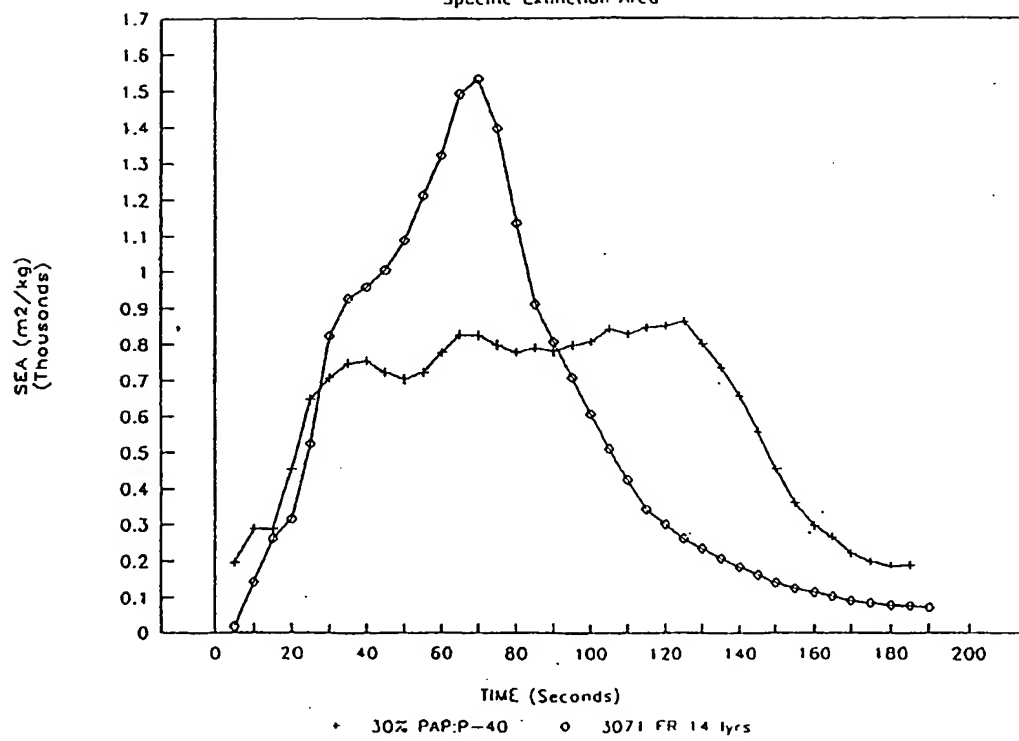


FIGURE 4

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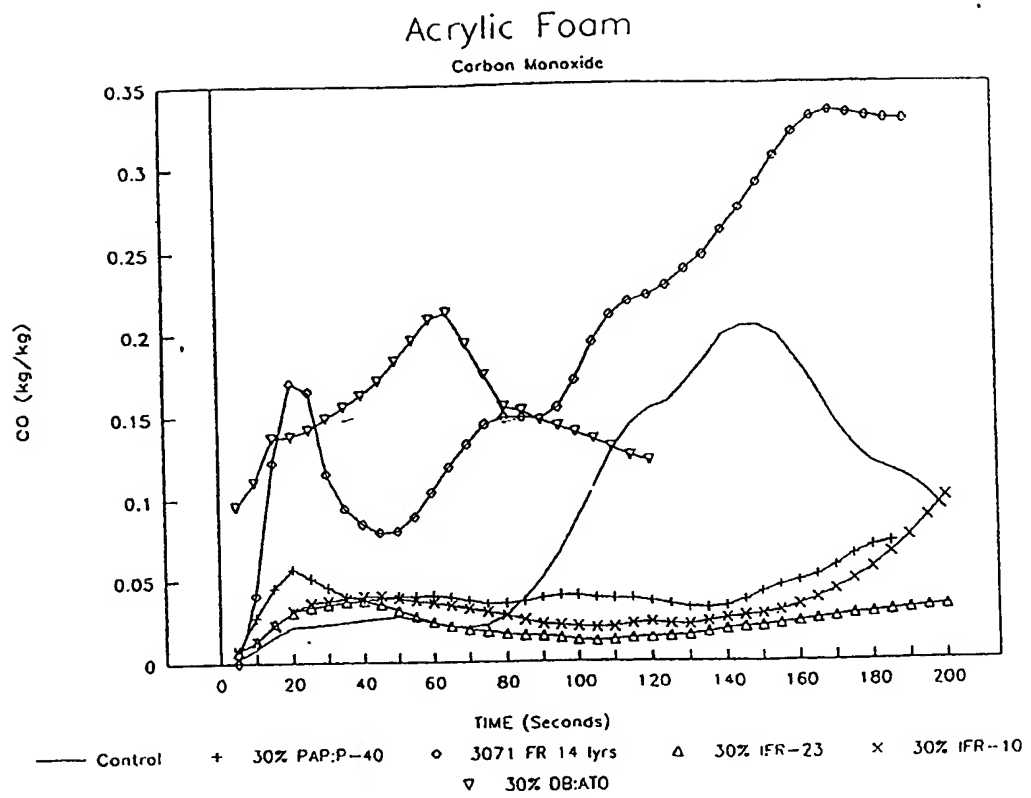


FIGURE 5

Acrylic Foam

Carbon Monoxide

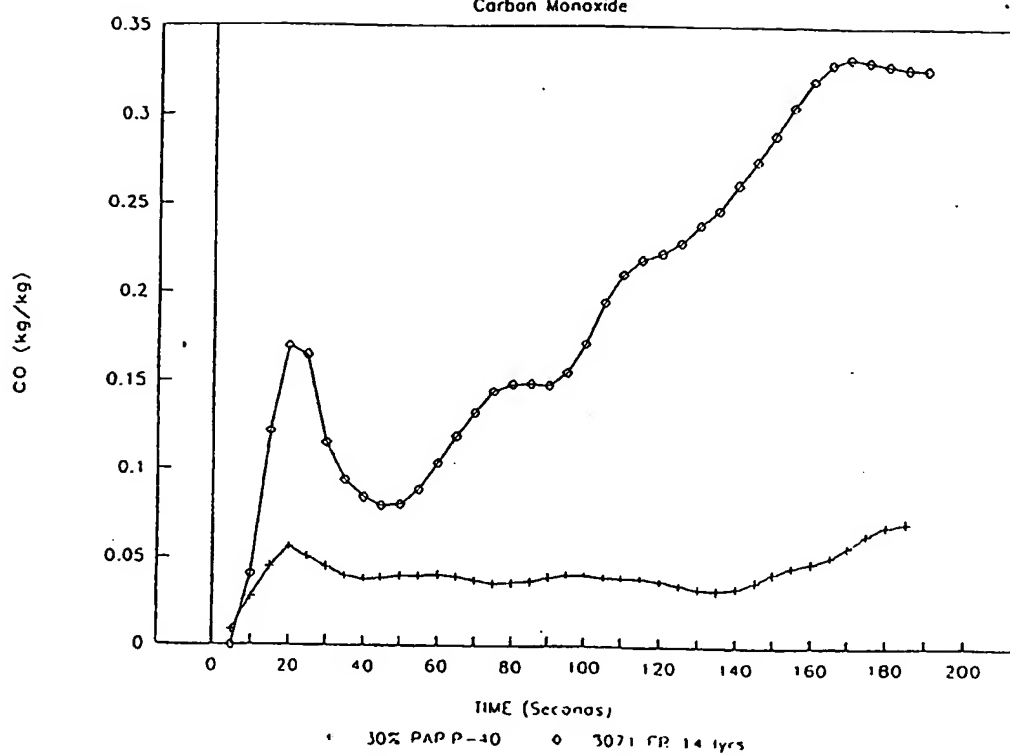


FIGURE 6

Flame Retardant Pressure
Sensitive Adhesives and Tapes

5 This invention relates to pressure sensitive
adhesive compositions containing non-halogen intumescent
flame retardant (NHIFR) additives and to flame retardant
pressure sensitive adhesive tapes.

10 Pressure sensitive adhesives find use, or have
potential uses, in a wide variety of applications, such
as in the automotive, aerospace, construction and
electrical markets, either in the form of tapes or as
adhesive coatings on other backings. For many of these
applications, good flame retardant properties are of
considerable importance. This performance has generally
15 been achieved by means of the incorporation of
halogenated, often brominated flame retardant additives
into the adhesive formulation, as disclosed for example,
in U.S. 4,061,826. Although efficient as flame
retardants, these types of materials have considerable
20 drawbacks in terms of smoke production and toxicity
concerns, relating both to combustion products and also
to disposal of the compounds themselves. Hence, there is
considerable momentum towards the reduction in use or
replacement of these flame retardants by zero halogen
25 alternatives.

30 A further limitation of the use of halogenated flame
retardants in pressure sensitive adhesives is that during
combustion they emit larger amounts of corrosive smoke.
Combustion products of halogen containing materials, in
particular HCl and HBr, contribute significantly to these
effects. The corrosivity of smoke is of particular
importance in electrical/electronic applications, since a
small fire involving halogenated insulation materials may
generate sufficient corrosive combustion products to
35 cause widespread damage to other equipment not directly
involved in the fire.

It has been suggested there is a synergistic
interaction between phosphorus based and halogenated

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flame retardant additives. However, a detailed review on this subject (Weil, E.D., in Flame retardancy of polymeric materials, eds. W.C. Kuryla and A.J. Papa, pp. 185ff, Marcel Dekker, New York, 1975) concludes that the evidence for phosphorus halogen synergism is too weak to call for any explanation.

NHIFR materials have been used in adhesives, but the majority of the systems disclosed do not comprise pressure-sensitive adhesives.

Known adhesives having flame retardants are commonly based upon epoxy resins e.g. JP 70108692 (Nitto Koseki KK) which describes the use of nitrogen containing phosphates such as melamine phosphate in epoxy adhesives, or polyurethanes e.g. U.S. 5,010,113 (Blount) which describes the use of urea-phosphoric acid salts as flame retardants for flexible polyurethane foams, with adhesives as one suggested application.

U.S. 4,496,685 (Sumitomo Chemical KK) discloses the use of a variety of phosphazenes in cyanoacrylate adhesives. Although flame retardant behaviour is mentioned as an issue, the main focus of the disclosure is directed towards the stabilisation properties of the phosphazenes resulting in improved storage stability of the resins.

SU 789556 (Channova) describes fire resistant adhesives consisting of butyl acrylate methacrylic acid copolymers with a mixture of borax, boric acid and ammonium phosphate as the fire retardant. However, the adhesives are not pressure sensitive adhesives.

The prior art does not disclose flame retardant pressure sensitive adhesive compositions.

According to one aspect of the present invention there is provided a pressure sensitive adhesive composition containing a non-halogen intumescent flame retardant.

The pressure sensitive adhesive compositions may be based on a wide variety of adhesives including rubber

based compositions, acrylic adhesive compositions and adhesive foams. The adhesive compositions have a wide variety of applications and are particularly suitable for use in the preparation of adhesive tapes.

5 The compositions of the invention possess an excellent combination of flame retardant and adhesive characteristics. In the case where solely NHIFR additives are used, reductions in smoke emission, and also in combustion toxicity and corrosivity, representing
10 improvements upon the art are conferred by a completely non-halogen composition. However, other flame retardants may be present and in the case where combinations of NHIFR and halogenated flame retardant additives are used together, a synergistic effect is seen in flammability
15 performance in rubber based compositions, with a surprising reduction in the tendency to produce burning drips during combustion. In addition, such combinations permit a reduction in the loading of halogenated flame retardant additive.

20 In one embodiment, the flame retardant is one or more NHIFR materials. Such materials normally contain up to three components: a carbonific, an acid forming catalyst, and a blowing agent. These three functions may be contained in only one or two chemicals. Such
25 materials usually contain phosphorus compounds, and often also contain compounds of nitrogen, and are known as P/N flame retardants.

30 In another embodiment, a blend of at least two flame retardant additives are used, with a combination of a NHIFR material with a halogenated, for example, a brominated additive.

A wide variety of non-halogen phosphorus/nitrogen flame retardants are useful in the invention.

35 Suitable flame retardants disclosed in EP 0115871 comprise a nitrogen containing oligomer and ammonium polyphosphate. An example is commercially available under the trade name SPINFLAM MF82.

Other suitable flame retardants, which are available under the trade name EXOLIT IFR-10 and EXOLIT IFR-23, comprise ammonium polyphosphate in admixture with a variety of other flame retardant synergists and coagents, fillers and pigments.

Other suitable flame retardants are disclosed in EP 0204027 and comprise mixtures of ammonium polyphosphate, melamine cyanurate and a hydroxyalkyl derivative of isocyanuric acid, at least partially in the form of a homopolymer. Examples of these materials are commercially available under the trade name MASTERFLAM.

Other suitable flame retardants are disclosed in EP 0413613A and comprise oligomeric phosphorus/nitrogen flame retardants containing a triazine nucleus, used in conjunction with ammonium polyphosphate.

Other suitable flame retardants are disclosed in British Patent Application No. 9208926.7 and comprise a polyphosphonamide derivative used in conjunction with ammonium polyphosphate.

Other suitable flame retardants are disclosed in British Patent Application No. 9223792.4 and comprise a polymeric salt containing both phosphorus and nitrogen, optionally used in conjunction with ammonium polyphosphate.

Another useful class are the phosphate salts of polyols such as pentaerythritol e.g. Great Lakes CN1197.

A useful class of halogenated flame retardants for use in combination with NHIFR materials are the halogenated polynuclear aromatic ethers, for example, decabromodiphenyl oxide (DBDPO).

The flame retardants are generally employed in amounts in the range 10 to 100 parts by weight, preferably 25 to 75 parts by weight, per 100 parts by weight of the pressure sensitive adhesive. In some cases, particularly when large amounts of flame retardant are employed, there will be a reduction in the tackiness of the adhesive composition. This problem may readily be

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overcome by overcoating such an adhesive composition with a thin layer e.g. 125 microns or less, preferably 5 to 10 microns, of adhesive containing no flame retardant additive or a low level of flame retardant additive which does not inhibit the tackiness of the adhesive. The overall two layer combination displays good tack and adhesive properties and surprisingly the presence of the top coat does not detract from the flame retardant performance.

The flame retardant(s) may be incorporated in the adhesive by conventional techniques such as ball-milling, and thereafter the pressure-sensitive adhesive composition may be applied to a substrate in order to confer adhesive properties thereon. The substrate may comprise a wide variety of materials such as plastics (including plastic films), paper, metal, wood, glass, cloth, etc. The substrate may have release properties (eg silicone coated paper on film) such that the adhesive may be transferred to a second substrate by a process of lamination followed by peeling of the first substrate. Depending on the size, shape and flexibility of the substrate, the adhesive composition may be applied by any conventional technique such as brushing, dipping, spraying etc, but most commonly the substrate is in the form of a flexible continuous web and the adhesive is applied by a method such as knife-coating, roller coating, extrusion, lamination, etc. The adhesive may be applied as a solution in organic solvent, as an aqueous emulsion or as a 100% solids formulation as appropriate. The adhesive layer may be crosslinked subsequent to application to the backing, eg by UV or e-beam curing, in order to modify its adhesive properties, in accordance with known techniques. Coated webs may be slit into narrow strips to form tapes, or otherwise converted into articles of the required dimensions.

A pressure sensitive adhesive tape using the adhesive of the invention may incorporate a variety of

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tape backings. For a particularly flame resistant tape,
 the backing may be glass cloth. Other useful backings
 include films of polyethylene terephthalate (PET),
 polyimide and polyolefin copolymers. The adhesive
 5 composition can be applied to the backing from solution,
 by hot melt coating, extrusion, or lamination of a
 preformed film from a release liner, in a variety of
 thicknesses ranging from a few microns to several
 millimetres, sufficient to provide the desired adhesion
 10 and other properties. Generally thin layer adhesives
 refer to those of about 125 microns or less. Foam
 adhesives are generally in the range 0.1 to 2.5mm. The
 backing may be coated with the adhesive in the form of a
 continuous web which is then slit in the longitudinal
 15 direction to form tapes of the desired width.

Tapes in accordance with the invention may be
 suitable for electrical, industrial, transportation,
 military and electronic applications. The tapes may be
 in a variety of forms e.g. simple coated substrate,
 20 double-sided etc.

The compositions of the invention may comprise any
 pressure-sensitive adhesive.

In one embodiment the base pressure sensitive
 adhesive material of a composition of the invention can
 25 be selected from a wide variety of rubber resin based
 materials. These comprise an elastomeric ingredient such
 as crude natural rubber, styrene-butadiene elastomer,
 polybutadiene, polyisobutylene and polysiloxane, and a
 tackifying resin such as glyceryl esters of hydrogenated
 30 resin, thermoplastic terpene resins, petroleum
 hydrocarbon resins, coumarone-indene resin, synthetic
 phenol resins, low molecular weight polybutenes and
 tackifying silicone resins. Some elastomers may be at
 least partially self tackified, as when low molecular
 35 weight fractions tackify the high molecular weight
 fractions of the elastomer. Generally a tackifying resin
 is included in a proportion of 40 parts to 150 parts per

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100 parts of base elastomer. Tapes using such adhesive compositions generally comprise a suitable backing coated with an approximately 1 mil thick layer of rubber resin adhesive containing up to 60% by weight of one or more flame retardant materials, and optionally contain pigments, fillers and/or tackifying agents.

The overall composition displays good flammability properties, as exemplified by performance in the UL510 flammability test, good adhesive characteristics and low smoke and toxic gas production upon combustion.

In a second embodiment, the base pressure sensitive adhesive is an acrylic adhesive. The acrylic pressure-sensitive adhesive material used in the invention can be selected from a wide variety of polymers and copolymers derived from acrylic and/or methacrylic acid, or ester, amide and nitrile derivatives thereof. Mixtures of different polymers and copolymers can be used. The polymers and copolymers preferably are of low Tg (eg < 0 deg.C) so that the mass of polymer is tacky at ambient temperatures, and no additional tackifying resin is required. Examples of useful acrylate based materials include homopolymers and copolymers of acrylic acid, methacrylic acid, isooctyl acrylate, acrylamide, methacrylamide, acrylonitrile, methacrylonitrile, methyl isoamyl acrylate, 2-ethyl hexylacrylate, and butyl acrylate.

For certain applications, particularly application to rough surfaces, it is necessary for the adhesive layer to be relatively thick e.g. 0.2 to 2.5mm. Such thick coatings of adhesive tend to be difficult and expensive to manufacture by traditional adhesive coating formulations and so called "foam" pressure sensitive adhesives have been developed. Such adhesives may be in the form of the foam having open or closed cells throughout the adhesive generated by frothing or a cellular structure may be achieved by the incorporation of hollow microspheres e.g. glass or polymeric

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microbubbles, into the adhesive formulation e.g. to occupy 20 to 65% of the volume of the adhesive. Examples of foam adhesives are disclosed in U.S. 4,223,067, U.S. 4,415,615 and EP 257984.

5 The pressure sensitive adhesive materials, particularly acrylate based materials, may also include glass bubbles, typically at levels up to 10 parts per 100 parts of acrylate material. They may also include ultra violet curing agents such as Irgacure 651 (Ciba Geigy),
10 typically at levels of up to 1 part per 100 parts of acrylate material to enable partial crosslinking to be accomplished by means of exposure to a UV source.

15 A typical foam tape of this invention consists of an acrylic adhesive foam, of thickness approximately 1mm, containing up to 60% by weight of a phosphorus/nitrogen flame retardant, glass microspheres and other coagents and optionally cured by ultraviolet light. The overall composition displays good flammability properties and low smoke and toxic gas production as exemplified by cone
20 calorimeter performance. The acrylic adhesive foam may be self-supporting, supported by a release liner or may be bonded to a backing.

25 A useful test for determining the flammability properties of adhesive tape compositions of this invention is the UL510 tape flammability test. In order to pass this test, burn times of less than 60 s must be observed following each of five successive 15 s bunsen applications to a vertical tape wrapped steel rod. In
30 addition there must be no emission of flaming drips and the length of burnt material must not extend to a paper flag places 10 inches above the point of impact of the bunsen flame.

35 A further useful method for classifying the flammability properties of the materials of this invention is evaluation on the cone calorimeter. This instrument is described in detail in "The cone calorimeter - a new tool for fire safety engineering",

ASTM Standardisation News, 18, 32-5, January 1990, and in ASTM test method E1354-90. Adhesive tape compositions were evaluated using a cone calorimeter at an external irradiant flux of 50 kW m⁻² and an exposed specimen surface area of 100 cm². In addition to flammability data such as rate of heat release, cone calorimeter evaluation yields data describing the smoke and toxic gas production behaviour of materials.

A useful method for flammability performance assessment is the Underwriters Laboratories UL94 test. This is a widely accepted test method and is commonly used by suppliers of flame retardants and flame retardant materials. In this test a vertically clamped specimen is ignited by a specified flame from a bunsen burner. For good performance in the test the specimen must self extinguish satisfactorily and not emit any flaming drips. UL94 defines the specimen size as 12.7cm (5 inches) long and 1.27cm (1/2 inch) wide. UL94 performance is thickness dependent and is quoted here for specimens of thickness 1mm.

Adhesive performance can be measured in a number of ways. One method used herein (Examples 16 and 20) was a rolling tube test, similar in form, although not corresponding to, the rolling ball tack test ASTM D 3121. In this test a tube of diameter 1.3 inches (3.3cm) and mass 138g was released from a point 6 inches (15cm) up a slope inclined at 10° to the horizontal. The lower end of the inclined slope impinged upon the surface of the specimen. When the tube was released, the distance it travelled along the specimen surface from the lower end of the incline before coming to rest was measured. Lower values in this test indicate better adhesive performance.

The ASTM D3121 rolling ball tack test was used in Example 5.

The invention will now be illustrated by the following Examples.

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The following general adhesive formulation was used in Examples 1 to 12 and batch sizes of 10g or 20g rubber were normally employed.

Table 1

5 General rubber adhesive formulation

	Ingredient	Parts (phr)
	Natural rubber smoked sheet, Goodyear	100
10	Piccolyte S115 Tackifier, Hercules	62
	Zirex (zinc resinate), Reichhold Chem	6
15	Ucar CKR 1634 Phenolic Resin, Union Carbide	12
20	Irganox 1010 antioxidant, Ciba Geigy	1
	Titanox 2020 TiO ₂ pigment NL Industries	0 or 16
25	Flame retardants	50 to 100
	Toluene	1200ml per 100g rubber

30 All the above ingredients were ball milled for at least 2 hours until well dispersed and then knife edge coated onto 1.2 mil (30 μ m) PET film (1.0 mil (25 μ m) film was used for Examples 8 to 12). Wet coating thicknesses of approximately ten times the final required adhesive layer thickness were used.

35 The coatings were dried in an oven at approximately 85°C for at least 10 minutes and then covered with silicone lining paper for storage. Samples were cut into $\frac{1}{4}$ " (19mm) wide strips and wrapped onto steel rods for UL510 flammability testing. All specimens tested in
 40 Examples 1 to 4 passed the UL510 test. Neither flaming drips nor burnt paper flags were observed in any of the tests described in Examples 1 to 4.

Example 1Adhesive tape formulations containing
Spinflam MF82/PP as a flame retardant

5 In this Example, a sample of Spinflam MF82/PP flame
retardant (Montefluos), supplied with mean particle size
approximately 40 microns, was jet milled to reduce its
particle size to around 5 microns. It was found that
10 this milling was required in order to produce a smooth
adhesive layer with no visible particles. In general,
for the 25 micron (1 mil) adhesive layer thickness used
here, a particle size of approximately 10 microns or less
was found to be suitable.

15 Flame retardant adhesive tape formulations were then
prepared as described above, containing jet milled
Spinflam MF82/PP as the P/N flame retardant, present at
the level of 75 to 100 parts. In some formulations 16
parts of TiO_2 was added.

Table 2UL510 flame tests on adhesive tapes
containing Spinflam MF82/PP

Spinflam loading (parts)	TiO_2 loading (parts)	coating thickness (mil) ($\times 25.4 \mu m$)	number of UL510 flame tests	results
100	0	1.0	3	all pass
100	0	1.1	5	all pass
100	16	1.0	4	all pass
75	0	0.9	4	all pass
75	16	0.9	3	all pass
75	16	1.3	3	all pass

Example 2Adhesive tape formulations containing
Exolit IFR-10 as a flame retardant

Using the generalised formulation, coating and test
procedure of Example 1, formulations containing various
loadings of another P/N flame retardant, Exolit IFR-10
(Hoechst-Celanese), were prepared and evaluated (see
table). 16 parts TiO_2 were added to all formulations.

Table 3UL510 flame tests on formulations containing
IFR-10 and TiO_2

loading (phr)	number of tests	results	coating thickness (mil) (x25.4 μ m)
75	3	all pass	0.6
	3	all pass	1.0
	3	all pass	1.6
70	3	all pass	0.7
	4	all pass	1.2
	4	all pass	1.8
60	3	all pass	0.9

As may be seen from Table 3, the requirements of the
UL510 flame test have been demonstrated for a range of
coating thicknesses at 70 and 75 parts IFR-10 loading.
Whereas Spinflam MF82/PP (supplied with 40 microns mean
particle size) requires jet milling before use in these
thin coatings, the Exolit IFR-10 (10 microns) was used as
supplied. In all cases smooth coatings were obtained
after ball milling the coating formulation in toluene for
at least 2 hours.

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Examples 3 and 4Adhesive tape formulations containing PNA
and PNB flame retardants

Two P/N flame retardants, PNA and PNB, were
 5 evaluated in adhesive coatings at 75 parts total flame
 retardant loading, using the generalised formulation of
 Example 1. In each case the flame retardant was a blend
 of the P/N material with ammonium polyphosphate (APP,
 Phoschek P40, Durham Chemicals) in a 2 : 3 ratio by
 10 weight, and 16 parts of TiO_2 were added. Both PNA and PNB
 materials were jet milled to around 5 microns particle
 size prior to formulation.

PNA is a triazine oligomer prepared as described in
 Example 3 of EP 0413613A. PNB is a polyphosphonamide
 15 prepared from phenylphosphonic dichloride and piperazine,
 as described in British Patent Application No. 9208926.7.

Table 4UL510 flame tests on formulations containing
PNA and PNB flame retardants

FR additive	loading (parts)	number of tests	results	coating thickness (mil) (x25.4 μ m)
2 : 3 PNA + APP	75 total	3	all pass	0.7
		4	all pass	1.0
		4	all pass	1.4
		2	all pass	1.8
2 : 3 PNB + APP	75 total	3	all pass	0.6
		3	all pass	1.1

Thus, both these flame retardant formulations meet
 the requirements of the UL510 flame test.

Example 5Adhesion measurements on IFR-10 formulation

Rolling ball tack adhesion tests (ASTM D3121) were performed to compare the relative adhesion of a NHIFR based adhesive tape (invention) with a brominated flame retardant based adhesive tape (comparative example). Good adhesion was obtained with both tapes (see Table 5).

The NHIFR tape contains 70 parts Exolit IFR-10 plus 16 parts TiO_2 in the adhesive (as in Example 2 above). The brominated tape contains Saytex 102 decabromodiphenyl oxide (Saytech) flame retardant (DBDPO) and antimony trioxide synergist (Anzon) in a 3 : 1 ratio at a combined loading of 60 parts plus 16 parts TiO_2 in the adhesive. Both tapes have an approximately 1 mil (25 μ m) thick adhesive layer on PET backing.

Table 5Rolling ball tack measurements on IFR-10 and DBDPO formulations

Flame retardant	Total flame retardant loading	Approximate roll distance (inches) (x25.4mm)
IFR-10	70 parts	5
DBDPO/ Sb_2O_3	60 parts	4

Example 6Cone calorimeter evaluation of smoke and toxicity (CO emission)

In order to assess the environmental advantages of a non-halogen adhesive tape over a halogenated formulation, smoke and carbon monoxide emissions were compared using a cone calorimeter for the two adhesive tapes from Example 5. Horizontal samples of 25 layers of tape and an irradiance level of 50 kWm^{-2} were employed. Test duration was 3 minutes.

Table 6
Smoke and CO Emission

Flame retardant	Smoke density (m ² /kg)		CO emission (kg/kg)	
	Peak	Mean	Peak	Mean
70 phr IFR-10	979	846	0.06	0.05
60 phr DBDPO/Sb ₂ O ₃	2224	1641	0.21	0.10

These data show a reduction of a factor of two or greater in smoke and toxic CO emission levels for the non-halogen adhesive tape formulation, when compared to the halogenated formulation.

Example 7

Corrosivity testing

Simple copper mirror corrosion tests have been performed on a NHIFR adhesive tape and a halogenated formulation. The tape formulations from Example 5 were used. For each material, approximately 1g of tape was burnt in a Stanton Redcroft FTA limiting oxygen index apparatus and the smoke sealed overnight in an FTB smoke chamber into which a copper mirror had been placed. Extensive pitting was seen on the mirror exposed to smoke from the brominated formulation, whereas no pitting was observed for the non-halogen formulation.

Example 8

Combinations of non-halogen and brominated flame retardants

Adhesive tapes utilising a NHIFR material, either jet milled Spinflam MF82/PP (JMSPP in the table), or Exolit IFR-10, or CN1197 (Great Lakes) in combination with Saytex 102 DBDPO (Saytech) were tested to UL510 (TiO₂ was not added).

Table 7

Combinations of non-halogen flame retardants with DBDPO

5	DB/NH ratio	DBDPO (phr)	non-halogen flame retardant (phr)		Sb ₂ O ₃ (phr)	Total FR (phr)	Wet coating thickness (mil) (x25.4μm)	UL510 passes/ tests
	4:1	48	JMSPP	12	0	60	20 15 11 7	1/3 3/3 3/3 3/3
	3:2	36	JMSPP	24	0	60	20 15 11 7	3/3 3/3 3/3 3/3
	3:2	36	CN1197	24	0	60	20 15 11 7	2/3 3/3 3/3 3/3
10	3:2	36	IFR10	24	0	60	20 15 11 7	1/3 2/3 3/3 3/3
	1:1	30	JMSPP	30	0	60	20 15	1/3 3/3

The data in the Table indicate that good performance in this flame test is obtained over a range of adhesive coating thicknesses using combinations of DBDPO with any of these three NHIFR materials at a total flame retardant level of 60 phr. The tendency to pass this test is reduced in some cases if the adhesive wet coating thickness is increased to around 20 mil (508μm).

The optimum performance is obtained using Spinflam MF82/PP with a ratio of around 3 DBDPO:2 Spinflam, and this particular blend demonstrates improved performance over combinations with lower or higher DBDPO:Spinflam ratios, and also over 3:2 blends of DBDPO with the other two NHIFRs evaluated in the Table. This particular synergistic effect was unexpected.

Example 9Comparative Example - brominated flame retardant

5 An adhesive tape formulation containing DBDPO and antimony trioxide (Anzon) synergist was prepared for comparison with the DBDPO/NHIFR blends examined in Example 8 above.

Table 8UL510 flame tests on brominated adhesive tapes

DBDPO parts	Sb ₂ O ₃ parts	Total FR (parts)	TiO ₂ parts	Coating thickness (mil) (x25.4μm)		UL510 passes/ tests
				wet	dry	
10 44.2	14.8	59	16	16	2.6	1/2
				11	1.9	1/2
				n/d	1.5	73/83
				6	1.1	2/2
				3	0.5	3/3

n/d = not determined

15 This type of brominated formulation suffers from the limitation that it has a tendency to fail the UL510 flammability test because of emission of flaming drips (see Table). The blends of DBDPO with NHIFRs examined in Example 8 above show improved performance over this comparative example.

Example 10Comparative example - no flame retardant added

20 A batch of adhesive containing no flame retardant and no TiO₂ was made and coated at about 1.1 mil (28μm) dry adhesive thickness. On the first ignition in UL510 testing it burned for 155 seconds with flaming drips, showing that the addition of a flame retardant is
25 necessary.

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Example 11Comparative example - alumina trihydrate

5 A formulation containing 100 parts of SB632 alumina trihydrate (Solem Industries) flame retardant, with no TiO_2 added was prepared. Adhesive thicknesses (dry) of 0.8, 1.1 and 1.8 mil (20, 28 and $46\mu\text{m}$) were coated on 1 mil ($25\mu\text{m}$) polyester. All tapes prepared had burn times greater than 80 seconds on first and second ignition, i.e. failed in UL510 tests.

10

Example 12Comparative example - Ceepree C-200

15 A batch was prepared containing 80 parts Ceepree C-200 (ICI) (no TiO_2 added). Ceepree C-200 is ceramic powder which is a mixture of glass frits, designed to melt and form a non-combustible coating when exposed to heat. The adhesive was coated at 20, 11, 7 and 5 mil (508, 254, 178 and $102\mu\text{m}$) wet thicknesses and the resulting tapes were tested to UL510. Each test failed, usually on the first ignition.

20

In the following Examples 13 to 17 two different acrylic adhesives were used.

Base Adhesive A

A copolymer of 98% isooctyl acrylate with 2% acrylic acid.

25

Base Adhesive B

A terpolymer of 93.75% isooctyl acrylate, 6% acrylic aid and 0.25% glycidyl methacrylate.

The phosphorus/nitrogen flame retardants used in the Examples were:

30

Exolit IFR-10 commercially available from Hoechst Celanese.

Poly(allylammonium) pyrophosphate (PAP).

(Example 1 of British Patent Application No. 9223792.4).

35

A comparative composition containing halogenated flame retardants with the flame retardant additive consisting of a total of 60 parts by weight, with respect

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to 100 parts acrylic adhesive, of a mixture of decabromodiphenyl oxide, antimony trioxide and titanium dioxide in the proportions 25 : 7 : 25 was used. This halogenated flame retardant mixture which is in accordance with U.S. 4,061,826 is referred to as DB.

Adhesive compositions were coated out onto the polyester backing by means of knife edge coating from a solvent consisting of 227.1 parts ethyl acetate and 177.2 parts n-hexane, with respect of 100 parts of Base Adhesive A or B.

Non-halogen adhesive compositions consisted of 100 parts Base Adhesive A or B with between 0 and 100 parts of phosphorus/nitrogen flame retardants and no other additives.

All formulations were ball milled for at least two hours to ensure good dispersion and then knife edge coated onto 1.2 mil (30µm) thick PET. Wet coating thicknesses of 10 mil (250µm) were employed, giving a final adhesive layer thickness of approximately 1 mil (25µm).

After drying, samples were cut into ¼ inch (1.9 cm) wide strips and wrapped onto steel rods for UL510 flammability testing.

Example 13

Adhesive formulations containing Exolit IFR-10 as the flame retardant additive.

Formulations were prepared containing 60 parts Exolit IFR-10 as the flame retardant additive in 100 parts Base Adhesive B. Mixing, coating and evaluation were performed as described above. UL510 flammability test results were as follows:

Number of tests performed	Results
3	All pass

Hence this formulation has been demonstrated to meet the requirements of the UL510 flammability test.

Example 14

Adhesive formulations containing Exolit IFR-23 as the flame retardant additive.

Formulations were prepared containing 60 parts Exolit IFR-23 as the flame retardant additive in 100 parts Base Adhesive A using the same methods as in Example 13. UL510 flammability test results were as follows:

10	Number of tests performed	Results
	3	All pass

Hence this formulation has been demonstrated to meet the requirements of the UL510 flammability test.

Example 15

Adhesive formulations containing PAP as the flame retardant additive.

Formulations were prepared containing 50 parts PAP as the flame retardant in Base Adhesive B using the same methods as in Example 13. UL510 flammability test results were as follows:

25	Number of tests performed	Results
	3	All pass

Hence this formulation has been demonstrated to meet the requirements of the UL510 flammability test.

Example 16

Adhesion testing of Exolit IFR-10 formulation.

Adhesion measurements were performed by means of the rolling tube tack test for a tape sample containing 100 parts base Adhesive A with 60 parts Exolit IFR-10 as the flame retardant adhesive and also for a tape sample containing 100 parts Base Adhesive A with 57 parts halogenated flame retardant additives as described above as a comparison.

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	Test sample	Additive loading/ parts	Approximate roll distance (inches)
	base adhesive A/IFR-10	60	6.5
5	base adhesive A/DB	57	4.0

Hence the adhesive properties of the 100 parts Base Adhesive A/60 parts Exolit IFR-10 formulation are comparable to that of the halogenated composition. The adhesion of the comparative halogenated composition is considerably in excess of that required to meet rolling ball tack tests such as ASTM D3121.

Example 17

Adhesive performance of top coated specimens versus non-top coated specimens.

Adhesion measurements, according to the rolling tube tack test, were performed for a specimen of 100 parts Base Adhesive A containing 60 parts IFR-10 with and without a top coat layer of non-flame retardant adhesive, Spray Mount (TM) adhesive, commercially available from Minnesota Mining and Manufacturing Company. The results were as follows:

Test specimen	Approximate roll distance (inches)
top coat	6.5
no top coat	> 20

The addition of a thin top coat layer (approximately 5 microns) of non-flame retardant, pressure sensitive adhesive considerably improves the tackiness of the composition.

Example 18

UL510 flammability performance of top coated specimens versus non-top coated specimens.

The tape samples of Example 17 were subjected to UL510 flammability testing and the results were as follows:

Test specimen	Number of tests	Classification
no top coat	3	all pass
top coat	3	all pass

Thus, the top coat layer has minimal effect upon flammability performance.

Example 19

Smoke and toxicity performance of halogenated and non-halogenated compositions.

Adhesive tape materials as described in Example 18 were evaluated on a cone calorimeter at an external irradiant flux of 50 kW m^{-2} . Smoke performance was evaluated by means of determination of the average specific extinction are (SEA, in $\text{m}^2 \text{ kg}^{-1}$). Toxicity performance was assessed by means of the average yield of carbon monoxide (CO, in kg per kg of sample burned) during the test. These data are as follows:

Flame Retardant	Smoke average SEA/ $\text{m}^2 \text{ kg}^{-1}$	Toxicity average CO/kg kg^{-1}
Exolit IFR-10	271	0.033
DB	724	0.135

Hence the non-halogen material displays much lower smoke and carbon monoxide production than the halogenated equivalent.

5	94.5/5.5	Isooctylacrylate/acrylic acid copolymer (total 100 parts)
	6 parts	Glass microspheres
10	0.30 parts	Irgacure 651 (Ciba Geigy)
	0.10 parts	Hexanediol diacrylate

Principal evaluations were conducted using the cone calorimeter. Materials were evaluated using an external
20 irradiant flux of 50 kW m^{-2} . It was found to be very difficult to remove both PET release liners from the specimen and avoid disintegration so as a matter of course samples were tested with one PET layer still in place, this forming the lower (unexposed) surface.
25 Materials were generally tested in duplicate or triplicate, dependent upon the repeatability of the first two runs. In all cases results are quoted as mean values for the runs undertaken.

a) Control
no flame retardant phosphorus/nitrogen containing
materials.

40 c) 30% IFR-10

a flame retardant commercially available from Hoechst Celanese under the trade name EXOLIT IFR-10.

d) 30% IFR-23

5 a flame retardant commercially available from Hoechst Celanese under the trade name EXOLIT IFR-23

e) 30% DB:ATO

30% decabromodiphenyl oxide:antimony trioxide [3:1]

f) 30% ATH

10 30% alumina trihydrate (Lonza Martinal OL-107C, stearic acid treated).

The following tape material was also tested:

g) 3071 FR

15 Avery Dennison Fastape 3071 acrylic tape. This material was examined as a 14 layer laminate of thickness approximately 1mm to correspond with the other specimens.

Example 20

UL94 Tests

20 UL94 tests were conducted on materials a) to f) as described above. For the control, not only did the drips ignite the gauze, but the flame continued to travel up the specimen (past the five inches mark). All samples containing flame retardants extinguished before the five inches mark.

Example 21

Cone Calorimeter Performance

25 Cone calorimeter tests were conducted on materials a) to g) and data for each of the materials is reported in the following Table.

Table

Material	RHR peak	RHR average	SEA average	CO average
Control	495	133	481	3.43
3071 FR	297	95	998	11.00
30% DB:ATO	187	87	1145	15.34
30% PAP:P-40	192	114	702	4.01
30% IFR-10	233	91	473	3.21
30% IFR-23	220	83	504	2.60
30% ATH	389	134	390	3.61

RHR peak = peak rate of heat release (kW m^{-2})

RHR average = average rate of heat release (kW m^{-2})

SEA average = average specific extinction area ($\text{m}^2 \text{kg}^{-1}$)

CO average = average yield of carbon monoxide (cg g^{-1})

In all cases average values are quoted over the range from ignition to ignition plus 3 minutes.

Rate of Heat Release

Rate of heat release data has been plotted in Figures 1 and 2. Figure 1 shows comparative data for each of the phosphorus/nitrogen materials alongside the 3071 FR material. Figure 2 shows the comparison between PAP:P-40 and 3071 FR with greater clarity.

These Figures illustrate that the three phosphorus/nitrogen flame retardants all show improved rate of heat release performance over the halogenated 3071 FR material. Of these, PAP:P-40 exhibits the best performance because, although it shows higher heat release during most of the test than the Exolit IFR materials, its peak RHR is lower and the time to peak RHR is longer. Both of these factors are advantageous in a real fire scenario, as they will decrease the flashover speed.

Similar comments can be applied to the comparison between PAP:P-40 and DB:ATO, as although the P/N compound shows higher heat release at longer time, the peak RHR and time to peak RHR values for the two materials are virtually identical, so their real fire performances would be expected to be comparable. The strength of the P/N materials is of course that this good rate of heat release performance is allied to excellent smoke and toxicity characteristics, as discussed below.

Specific Extinction Area

Specific extinction area data is illustrated in Figures 3 and 4. Figure 3 shows plots for all the materials evaluated with the exception of ATH. Figure 4 compares the behaviour of PAP:P-40 with that of 3071 FR. It is evident that all of the P/N additives show much better performance as regards smoke propensity than their halogenated counterparts, with Exolit IFR-10 exhibiting marginally the best performance. Whilst the P/N additives are all higher smoke materials than ATH at this loading, ATH is a very poor performer in terms of rate of heat release. The key advantage of P/N materials is that they show desirable properties in all fire characteristics.

Carbon Monoxide

Figure 5 shows plots for all materials with the exception of ATH; Figure 6 providing a comparison between PAP:P-40 and 3071 FR. The halogenated materials, either containing DB:ATO or 3071 FR, both produce very high yields of carbon monoxide throughout the test. This compares with the very low yields of carbon monoxide generated by the phosphorus/nitrogen intumescent type flame retardants. Although there are a multiplicity of toxic species in the cocktail of combustion products that arise from any fire, carbon monoxide is invariably of most importance due to its presence in large amounts and human inability to detect it by means of odour, irritancy etc.

The overall results demonstrate the great utility of phosphorus/nitrogen flame retardants, in that they provide a route to low heat release materials, comparable in this respect with halogenated additives, whilst showing excellent smoke and carbon monoxide performance, comparable to inorganic additives, such as, alumina trihydrate.

Example 22

Adhesive Tack Performance of Acrylic Foams

Adhesive tack measurements were performed by means of the rolling tube tack test. A clean tube was released onto the foam surface from a set distance at a set height and the distance covered by the tube before coming to rest was measured as described above. Specimens consisted of strips of width 1 inch (2.54cm), securely fastened to the bench surface. Rolling tube results are listed.

Adhesive Tack Performance of Acrylic Foams

Material	Number of tests	Average roll distance/mm
Control	5	19
30% PAP:P-40	4	17
30% IFR-10	4	21
30% DB:ATO[3:1]	4	43

The results demonstrate the phosphorus/nitrogen flame retardant additives do not seriously detract from the adhesive tack of the composition, with the PAP:P-40 additive actually improving the tack. Furthermore, the phosphorus/nitrogen additives show considerably improved adhesive tack test performance over the halogenated flame retardant composition.

Example 23Peel Adhesion and Static Shear Performance

Four tests were performed on a variety of specimens:

- a) 90° peel adhesion, 20 minute dwell
- b) 90° peel adhesion, 72 hour dwell
- c) static shear, 1 inch x $\frac{1}{2}$ inch (2.54cm x 1.27cm), 1kg, room temperature, and
- d) static shear, 1 inch x $\frac{1}{2}$ inch (2.54cm x 1.27cm), 500g, 70°C.

Test methods were as follows:

Peel adhesion

A 0.5 inch (1.27cm) wide strip of foam tape was applied to a clean 2 inch x 6 inch (5.1cm x 15.2cm) stainless steel panel and rolled down with a 4.51b (2.04kg) roller. The liner was removed and a 0.005 inch (0.13mm) thick anodized aluminium foil strip was applied. This was rolled down once with a 151b (6.8kg) roller and the bonded assembly was then housed in a constant temperature and humidity room for the specified dwell time (20 minutes or 72 hours). Peel adhesion was then measured on an Instron tensile tester with a jaw separation rate of 12 inch/min. (30.5cm/min.). The value obtained is quoted in oz/0.5 inch.

Static Shear

A 1 inch x $\frac{1}{2}$ inch (2.54 x 1.27cm) piece of foam tape was applied to a clean stainless steel panel and rolled down with a 4.51b (2.04kg) roller. The liner was removed and an anodized aluminium foil strip applied as above. The sample was then housed in a constant temperature and humidity environment for 24 hours prior to testing. A loop was formed from the aluminium strip (stapled together) from which the specified weight was hung (either 1kg or 500g). The time to failure was recorded or until 10,000 minutes was reached.

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Tape samples were prepared from the adhesive formulation described above with the flame retardants and amounts reported in the following Table:

Sample	Flame Retardant	Loading/ %
(i)	None	-
(ii)	DBDPO:ATO(3:1)	19
(iii)	DBDPO:ATO(3:1)	30
(iv)	DBDPO:ATO:ATH(2:1:1)	20
(v)	IFR-10	30
(vi)	IFR-10	40
(vii)	IFR-10	50
(viii)	ATH	30
(ix)	ATH	40
(x)	ATH	50

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The peel adhesion and static shear results are reported in the following Table:

Sample	Test (a)	Test (b)	Test (c)	Test (d)
(i)	66	110	10,000+	10,000+
(ii)	92	121	10,000+	10,000+
(iii)	not tested	40	10,000+	10,000+
(iv)	55	200	10,000+	10,000+
(v)	62	97	10,000+	10,000+
(vi)	62	99	10,000+	10,000+
(vii)	48	114	10,000+	10,000+
(viii)	43	93	10,000+	10,000+
(ix)	42	69	10,000+	10,000+
(x)	18	35	10,000+	10,000+

The data demonstrates that acrylic foams containing a P/N flame retardant such as Exolit IFR-10 show excellent adhesion performance, even at high loadings. Peel adhesion performance is considerably better for the P/N flame retardant than for either the halogenated flame retardant or ATH. Static shear results are good for all materials.

CLAIMS

1. A pressure sensitive adhesive composition containing a non-halogen intumescent flame retardant.
2. A pressure sensitive adhesive composition as claimed in Claim 1 which comprises a rubber elastomer selected from crude natural rubber, styrene-butadiene, polybutadiene, polyisobutylene and polysiloxane.
3. A pressure sensitive adhesive composition as claimed in Claim 1 or Claim 2 which additionally comprises a tackifying resin.
4. A pressure sensitive adhesive composition as claimed in Claim 3 in which the tackifying resin is present in an amount of from 40 to 150 parts by weight per 100 parts by weight of rubber elastomer.
5. A pressure sensitive adhesive composition as claimed in Claim 3 or Claim 4 in which the tackifying resin is selected from glyceryl esters of hydrogenated resin, thermoplastic terpene resins, petroleum hydrocarbon resins, coumarone-indene resins, synthetic phenol resins, polybutenes and silicone resins.
6. A pressure sensitive adhesive composition as claimed in Claim 1 comprising an acrylic pressure sensitive adhesive containing a non-halogen phosphorus/nitrogen flame retardant additive.
7. A pressure sensitive adhesive composition as claimed in Claim 6 in which the acrylic adhesive is selected from homopolymers and copolymers of acrylic acid, methacrylic acid, isooctyl acrylate, acrylamide, methacrylamide, acrylonitrile, methacrylonitrile, methyl isoamyl acrylate and 2-ethyl hexylacrylate.
8. A pressure sensitive adhesive composition as claimed in Claim 6 or Claim 7 in which the acrylic adhesive comprises polymeric or glass microbubbles dispersed throughout the composition.

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9. A pressure sensitive adhesive composition as claimed in Claim 8 in which the microbubbles have an average diameter of 10 to 200 microns and occupy from 20 to 65% by volume of the adhesive.

5 10. A pressure sensitive adhesive composition as claimed in any preceding Claim in which the flame retardant additive comprises ammonium polyphosphate.

11. A pressure sensitive adhesive composition as claimed in any preceding Claim in which the flame retardant
10 additive comprises a nitrogen containing oligomer and ammonium polyphosphate.

12. A pressure sensitive adhesive composition as claimed in Claim 11 in which the flame retardant additive additionally comprises melamine cyanurate and a
15 hydroxyalkyl derivative of isocyanuric acid, at least partially in the form of a homopolymer.

13. A pressure sensitive adhesive composition as claimed in any one of Claims 1 to 10 in which the flame retardant additive comprises a phosphorus containing oligomer
20 having a triazine nucleus.

14. A pressure sensitive adhesive composition as claimed in any one of Claims 1 to 10 in which the flame retardant additive comprises a polyphosphonamide containing oligomer having a triazine nucleus.

15. A pressure sensitive adhesive composition as claimed in any one of Claims 1 to 10 in which the flame retardant additive comprises a polymeric salt containing both
25 phosphorus and nitrogen.

16. A pressure sensitive adhesive composition as claimed in Claims 1 to 10 in which the non-halogen intumescent
30 flame retardant comprises a phosphate salt of a polyol.

17. A pressure sensitive adhesive composition as claimed in any preceding Claim which additionally comprises a further flame retardant.

18. A pressure sensitive adhesive composition as claimed
35 in Claim 17 in which said further flame retardant is halogenated.

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